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Radiation dose dependent change in physiochemical, mechanical and barrier properties of guar gum based films

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ABSTRACT

Mechanical and water vapor barrier properties of biodegradable films prepared from radiation processed guar gum were investigated. Films prepared from GG irradiated up to 500 Gy demonstrated significantly higher tensile strength as compared to non-irradiated control films. This improvement in tensile strength observed was demonstrated to be due to the ordering of polymer structures as confirmed by small angle X-ray scattering analysis. Exposure to doses higher than 500 Gy, however, resulted in a dose dependent decrease in tensile strength. A dose dependent decrease in puncture strength with no significant differences in the percent elongation was also observed at all the doses studied. Water vapor barrier properties of films improved up to 15% due to radiation processing. Radiation processing at lower doses for improving mechanical and barrier properties of guar based packaging films is demonstrated here for the first time.

1. Introduction

In the past twenty years, the production and use of plastics in the world has increased enormously to about 200 million tons per year. Packaging constitutes the largest market for plastics, amounting to over 12 million tons per year (Rhim and Perry, 2007). Increasing demand for synthetic packaging materials has put tremendous pressure on the environment because of their poor biodegradability and non-renewability (Ghasemlou, Khodaiyan, Oromiehie, & Yarmand, 2011). This has lead to a search for packaging materials that are biodegradable as well as recyclable (Mangiacapra, Gorrasi, Sorrentino, & Vittoria, 2006). One of the alternatives is the development of packaging material from biopolymers (i.e. protein, polysaccharide and lipid) that are biodegradable, non-toxic and derived from completely renewable resources. Among the biopolymers, polysaccharides are the most widely used for preparation of packaging films.

Widely studied polysaccharides for edible or biodegradable films are: starch, chitosan, carrageenan, and galactomannans. In packaging industry galactomannan is used as edible coating because it forms very thick aqueous solution at low concentration (Cerqueira et al., 2011), is an excellent emulsifier and non-toxic (Cerqueira, Lima, Teixeira, Moreira, & Vicente, 2009). Guar gum (GG) is a type of galactomannan, derived from endosperm of an annual legume plant *Cyamopsis tetragonoloba*. India accounts for 80 percent of world production of GG. It is a hetropolysaccharide of a mannose (i.e. (1-4)-linked β-D-mannopyranose) backbone with galactose side groups ((1-6)-linked α-D-galactopyranose) (Aydinli, Tutas, & Bozdemir, 2004; Das, Ara, Dutta, & Mukherjee, 2011; Martins, Cerqueira, Souza, Carmo, & Vicente, 2010). It is mainly used in paper, food and pharmaceutical industries (Chudzikowski, 1971).

Major limitations in the use of biopolymers as packaging materials are their relatively poor mechanical and barrier properties such as tensile strength and water vapor transmission rate as compared to their non-biodegradable counterparts (Cha and Chinnan, 2004; Kang and Min, 2010; Petersson and Oksman, 2006). This has resulted in a greater focus on improving the properties of these polymers to match the commercially available packaging material. Various chemical and physical methods have been used for improving biopolymer film properties. Among the physical methods, addition of plasticizer for improving mechanical properties of biodegradable films has been extensively reported. This increases the percentage elongation of films by forming hydrogen bond with the polymer and reducing polymeric interactions. Polysaccharide based films are commonly plasticized with polyols such as glycerol (Garcia, Ribba, Dufresn, Aranguren, & Goyanes, 2011).

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Among the chemical methods, chemical modification of guar galactomannan with benzamide for preparation of water resistant films has been recently reported (Das et al., 2011). Mikkonen et al. (2007) used enzymatic depolymerization for improving mechanical properties of GG film. Gamma irradiation has been widely used for the improvement of mechanical properties of pectin (Kang, Jo, Lee, Kwon, & Byun, 2005), starch (Kim, Jo, Park, & Byun, 2008) and calcium caseinate edible films (Vachon et al., 2000). Use of gamma irradiation for GG depolymerization has been previously reported (Gupta, Shah, Sanyal, Variyar & Sharma, 2009). There are several advantages associated with gamma irradiation such as convenience, eco friendly nature of the process (Hwang, Jung, Kuk, Choi, & Nho, 2010) and short processing time.

Physical treatments such as gamma irradiation could possibly change conformations of polymers in solution. Several investigations have shown that the conformation and morphology of polymer chains affect the physical properties of the polymer. Polymer chain conformation and chain correlation can be estimated by small angle X-ray scattering (SAXS) (Winokur, Skotheim, Elsenbaumer, & Reynolds, 1998). SAXS arises from the fluctuations of electron density in a mesoscopic length scale (1–100 nm) in a specimen and hence scattering profile contains the information about the size/size distribution and shape of the inhomogeneities (Glatter and Kratky, 1982).

To the best of our knowledge, no reports exist till date on the assessment of the effects of gamma irradiation on mechanical and barrier properties of GG based films. The main objective of this work was to study the effect of irradiation on physiochemical properties of GG and to determine the impact of these properties on the mechanical and barrier properties of films prepared from the irradiated GG.

2. Materials and methods

2.1. Purification of GG

Purification of guar gum was carried out as per procedure detailed earlier by Jumel, Harding, and Mitchell (1996). In brief, 2.5 g of GG (Merck India ltd.) was dissolved in 250 ml of distilled water by using shear mixer (Omni mixer, Sorvall, USA) at speed 2 for 2 min. Solution obtained was kept overnight on magnetic stirrer at room temperature (25 ± 2 °C). Resulting solution was centrifuged at 9000 rpm for 30 min for removal of insoluble impurities. Ethanol was added to supernatant in the proportion of 2:1 and resulting mixture was kept overnight for precipitation of GG. The precipitate obtained was freeze dried to obtain dry purified GG powder. Yield obtained by above purification procedure was 60%.

2.2. Irradiation of GG

Purified GG as dried powder was exposed to gamma radiation processing using a ^{60}Co gamma irradiator having dose rate of 4.1 kGy/hr (GC-5000, BRIT, India) at room temperature. GG was subjected to a dose of (0.25, 0.5. 0.75, 1, 5, 10, 25 and 50 kGy). In addition, films prepared from control unirradiated GG were subjected to gamma radiation to a dose of (1, 5, 10, 25, 50 and 100 kGy) after 7 days of conditioning.

2.3. Viscosity average molecular weight analysis by Ostwald viscometer

Viscosity average molecular weight of GG post irradiation was measured using Ostwald's viscometer at constant temperature of 24 ± 1 °C. 0.1% w/v aqueous solution was prepared from control and irradiated GG and specific viscosity (η_{sp}) was obtained using following Eq. (1):

$$[\eta_{sp}] = \frac{(t - t_0)}{t_0} \quad (1)$$

where t = flow time of a polymer solution through viscometer; t_0 = flow time of the pure solvent through the same viscometer.

Intrinsic viscosity (η) was then calculated from η_{sp} using following Eq. (2):

$$[\eta] = \frac{[\eta_{sp}]}{c} \quad (2)$$

where c = polymer concentration.

Viscosity-average molecular weight (M_v) was calculated from η (Eq. (3)) (Vega, Lima, & Pinto, 2001).

$$[\eta] = KM_v^a \quad (3)$$

where K and a are the parameters that depend on the solvent-polymer pair. The a and K values used for guar galactomannan were 0.72 and 5.13×10^{-4}, respectively (Beer, Wood, & Weisz, 1999).

2.4. Molecular weight and polydispersity index analysis by gel permeation chromatography

Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) (M_w/M_n) were determined by gel permeation chromatography (GPC) using a column (300 mm length × 4.6 mm I.D.), 5u Biobasic SEC-1000, Thermo Scientific, UK). The HPLC system (Ultimate 3000, Dionex Corporation, Germany) having differential refractive index detector (RI-101, Shodex Corporation, USA) was used. The mobile phase was deionized water (Millipore, Bedford, MA) and the flow rate was fixed at 0.6 mL/min. All GG samples were injected (20 μL) as their aqueous solutions at concentrations of 0.2% (w/v) which were centrifuged at 12,000 rpm for 15 min prior to analysis. The column was calibrated using pullulan standards (Fluka Analytical, St. Louis, USA) ranging from molecular weights of 6000 to 2,560,000 Da. Pullulan standards were analyzed using similar HPLC conditions described above.

Number average molecular weight (M_n) was calculated by following Eq. (4):

$$M_n = \sum \left(\frac{N_i}{\sum N_i} \times M_i \right) \quad (4)$$

where N_i = detector response at a particular time

$$\sum N_i = \text{Total detector response}$$

M_i = Molecular weight at given time.

Weight average molecular weight was calculated by following Eq. (5):

$$M_w = \sum \left(\frac{A_i \times M_i}{\sum A_i} \right) \quad (5)$$

where $A_i = N_i \times M_i$

Based on M_n and M_w, PDI was calculated using equation given below:

$$\text{PDI} = \frac{M_w}{M_n} \quad (6)$$

2.5. Determination of mannose to galactose ratio of GG by HPLC

Control and irradiated GG samples were hydrolyzed by 1 N sulphuric acid at 90 °C for 5 h. After hydrolysis samples were neutralized using barium hydroxide and barium sulfate precipitates

thus formed were removed by centrifugation at 12,000 rpm for 10 min. Supernatants were freeze dried and dried powder obtained was dissolved (1% w/v) in 70:30::acetonitrile:water and filtered through 45 μm filter prior to analysis. Samples were then analyzed using HPLC system (Quaternary gradient pump, PU-2089 plus, Jasco, Japan) equipped with High Q silica base amino column (Hi Q SIL NH_2, KYA TECH Corporation, Japan) with column dimension (4.6 mm I.D. × 250 mm L) and refractive index detector (RI-2031 plus, Jasco, Japan). All samples were analyzed by ChromPass software (Jasco, Japan). The mobile phase was 80:20::acetonitrile:water with a flow rate of 1 ml min^{-1}. 100 μL of all GG samples were injected. Standard curves for both galactose and mannose were made from 0.25 mg to 1 mg using similar HPLC conditions described above. Linear regression equations for both standards were then obtained. In hydrolyzed GG samples, galactose and mannose content was calculated using linear regression equations obtained above and G/M ratio was then obtained.

2.6. Preparation of GG films

1.5 g of GG was added into 150 mL water along with 0.5 mL of glycerol (40% w/w of GG) as plasticizer and kept overnight at room temperature (25 ± 2 °C) on magnetic stirrer. Solution thus obtained was centrifuged at 3000 rpm for 15 min for the removal of air bubbles. 150 ml of solution was poured and spread evenly onto surface of glass plate (21 cm × 21 cm), having removable boundary of insulating tape. Plates were then kept in oven at 80 °C for 8 h for drying. Dried GG films were conditioned at 50% relative humidity at room temperature (25 ± 2 °C) for 7 days. After conditioning films were pealed and subjected to physical and mechanical analysis. In another set of experiment, films were also prepared from unpurified native guar gum in the same manner as above.

2.7. Physical and mechanical properties of GG films

GG films were cut into strips of dimension 2 cm × 15 cm. Micrometer (103–131, Mitutoyo, Japan) was used to determine film thickness. Measurements were randomly taken at three different locations on each film strip. The mean value of thickness of each strip was used in calculations for the tensile strength, puncture strength and % elongation of same strip. Mechanical properties of films were analyzed using a Texture analyzer (TA.HD Plus, Stable Micro Systems). The American Society of Testing and Materials (ASTM) standard method D882-10 was used to measure the tensile strength (TS), Young's modulus and percent elongation at break (% E) of films. Puncture strength of films (5 cm × 2 cm) were determined by 2 mm needle probe having test speed of 30 mm/min. Water vapor transmission rate (WVTR) of GG films were determined by using round cups having 100 mL volume capacities and having 120 cm^2 area of mouth. It was filled with 60 mL of distilled water and sealed with GG film using adhesive tapes and assembly was kept in desiccators at 25 ± 2 °C. 100% RH gradient was used and maintained by using excess of H_2SO_4. The mass of water lost from the cup was monitored as a function of time, and the WVTR was calculated from the steady-state region. Color of films were determined using a colorimeter (CM-3600d Konica Minolta sensing Inc., Japan) by measuring L^*, a^* and b^* values. Instrument was calibrated using a white tile supplied along with the equipment. Source used was D65 with observer set at 10 degrees. Opacity is a measure of the extent of light passing through any material. Opacity of films was determined using Hunter lab method, as the relationship between reflectance of each sample on black standard and the reflectance on white standard using Eq. (7) as given below:

$$\text{Opacity} = (Y_b/Y_w) \times 100 \quad (7)$$

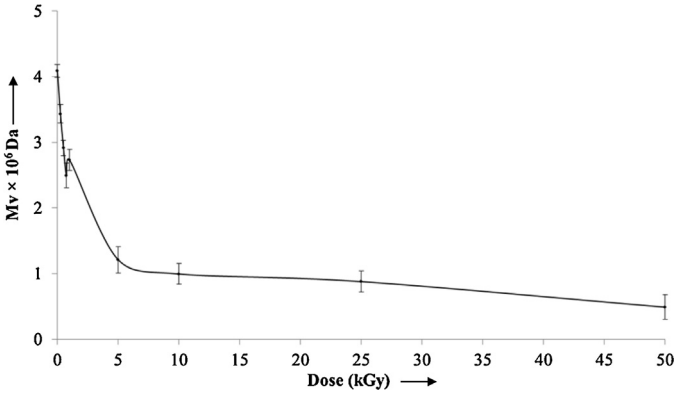

Fig. 1. Effect of gamma irradiation on viscosity average molecular weight (M_v) of GG.

All measurements were carried out in triplicates at room temperature 25 ± 2 °C and 50% relative humidity.

2.8. Small angle X-rays scattering measurements

SAXS measurements were performed on the aqueous solution of the control, 500 Gy and 50 kGy dose treated polymer at a lab based SAXS setup using CuKα source. Size of the incident photon beam on the sample was 0.4 mm diameter. The SAXS detector was mounted at a sample-to-detector distance of 1.07 m, corresponding to a q-range of 0.1–2.5 nm^{-1}. The magnitude of the scattering wave vector, q equals:

$$q = 2 \sin\theta/\lambda = q/2\pi \quad (8)$$

where 2θ is the scattering angle and λ = 0.154 nm the used wavelength.

2.9. FTIR analysis of guar gum films

Spectra of guar gum films were scanned in the range of 4000–600 cm^{-1} on a FTIR (FT/IR 4100, Jasco) spectrometer. ATR assembly was used for obtaining FTIR spectra. Films were directly pressed on ATR assembly and spectra were recorded. 40 scans were taken for each film sample.

2.10. Statistical analysis

DSAASTAT ver. 1.101 by Andrea Onofri was used for statistical analysis of data. Three samples were taken for every treatment and each sample was further analyzed in triplicates. Data was analyzed by Analysis of variance (ANOVA) and multiple comparisons of means were carried out using Duncan's multiple range test.

3. Result and discussion

3.1. Effect of gamma irradiation on physio-chemical properties of GG

Control GG had an intrinsic viscosity (η_{sp}) of 2.95 and viscosity average molecular weight (M_v) of 4.09 × 10^6 Da. Radiation processing resulted in significant ($p < 0.05$) reduction in viscosity average molecular weight (M_v) of GG (Fig. 1). Reduction in M_v due to irradiation was in a non-linear dose dependent manner. GG irradiation resulted in rapid decrease in M_v up to 2 kGy followed by a much slower decrease at higher doses. M_v of GG reduced to 1.5 × 10^6 Da and 4.9 × 10^5 Da at 2 and 50 kGy, respectively (Fig. 1). Similar results were also obtained by Jumel et al. (1996) during irradiation processing of GG.

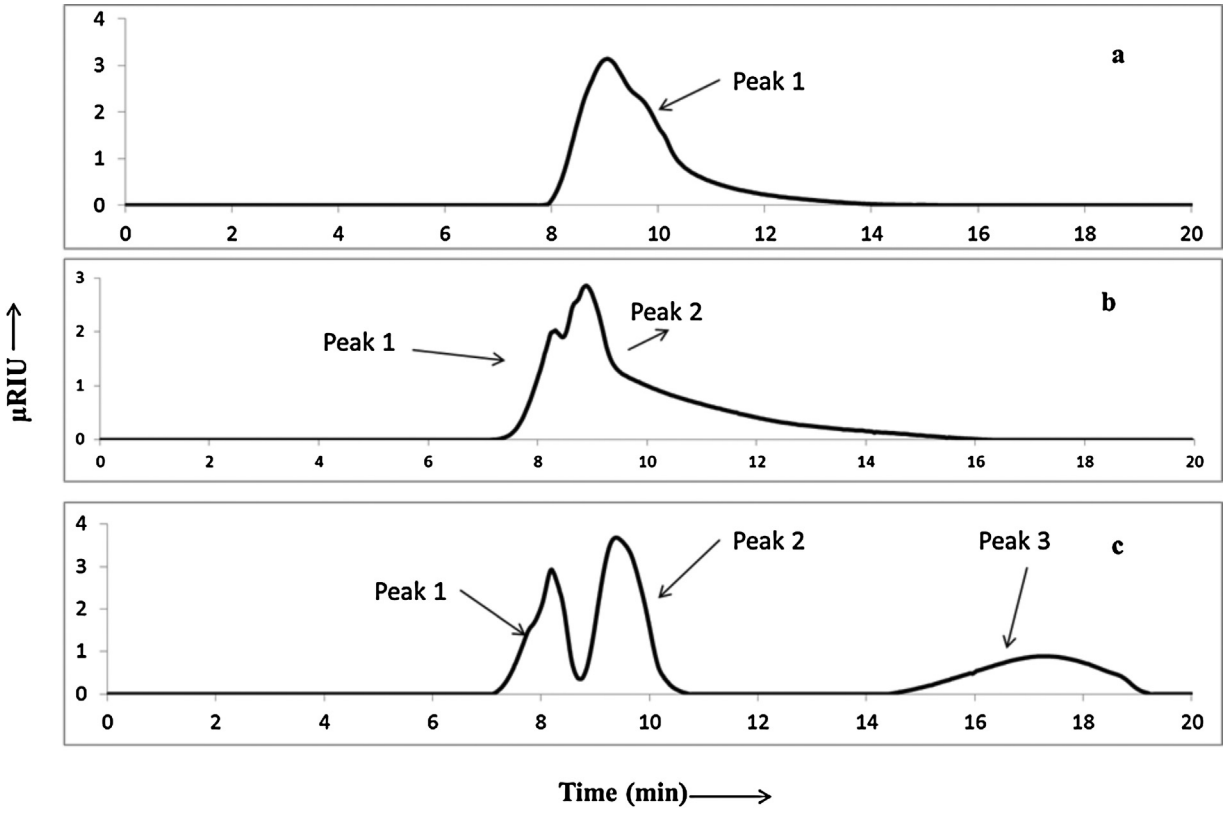

Fig. 2. A representative gel permeation chromatogram (GPC) of GG samples: (a) control unirradiated GG; (b) GG irradiated to a dose of 1 kGy; (c) GG irradiated to a dose of 50 kGy.

GG samples were further analyzed using gel permeation chromatography (GPC) for evaluation of weight average molecular weight (M_w). GPC chromatogram for the control GG showed a single peak corresponding to M_w of 4×10^6 Da (Fig. 2a). In earlier studies on guar gum M_w was reported to be 2.7×10^6 Da by Jumel et al. (1996). Hence results obtained are in accordance with published data. Two peaks (Peaks 1 and 2) were observed in GPC chromatograms at doses up to 1 kGy for GG irradiation (Fig. 2b). Peaks 1 and 2 had M_w of 4×10^6 and 2.5×10^6 Da, respectively. M_w of these peaks was comparable to that of control GG. At low doses (up to 1 kGy) of irradiation a disruption of supramolecular structures of GG polymer rather than depolymerization as reported by Jumel et al. (1996) could possibly explain the two peaks observed in GPC chromatograms. A third peak (Peak 3) having a M_w 2×10^5 Da was also observed in GPC chromatograms beyond the irradiation dose of 1 kGy (Fig. 2c). Appearance of this peak in the chromatogram could be attributed to the formation of depolymerized polymer as a result of gamma radiation. Radiation processing up to a dose of 5 kGy resulted in significant ($p < 0.05$) increase in relative area of peak 2 with corresponding decrease in area of peak 1. However, beyond radiation dose of 5 kGy a significant ($p < 0.05$) dose dependent increase in relative area percent of peak 3 with a decrease in Peaks 1 and 2 was observed (Fig. 3). Results from both viscosity as well as gel permeation chromatography suggested a gradual degradation of GG during irradiation. Similar results for radiation induced degradation of GG were earlier reported by Gupta et al. (2009).

Polydispersity index (PDI), which is a measure of molecular weight distribution of any polymer sample, was also calculated for control and irradiated GG samples. A radiation dose dependent increase in PDI of GG samples was observed (Fig. 4). PDI of control GG was 1.05 which increased to 1.16 at 1 kGy and 1.29 at 50 kGy for irradiated GG (Fig. 4). Jumel et al. (1996) have also reported a wide molecular weight distribution of irradiated GG samples as compared to non-irradiated controls. Increase in PDI with irradiation dose could possibly be explained by random phenomenon of radiation induced degradation of GG polymer.

M/G ratio of control GG was found to be 1.6:1 which is in accordance with results reported previously by Cunha, Castro, Rocha, Paula, and Feitosa (2005). No statistically significant ($p < 0.05$) differences were observed in M/G ratio of GG samples due to radiation processing in the present study. M/G ratio of galac-

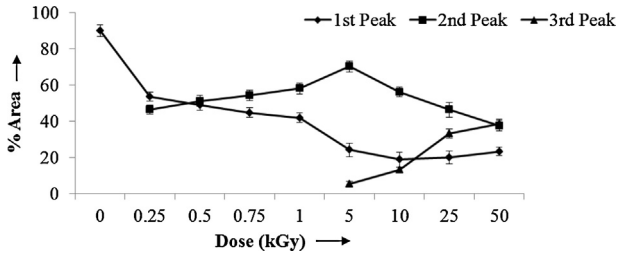

Fig. 3. Variation of relative percent area of peaks observed in gel permeation chromatography (GPC) of GG with radiation dose.

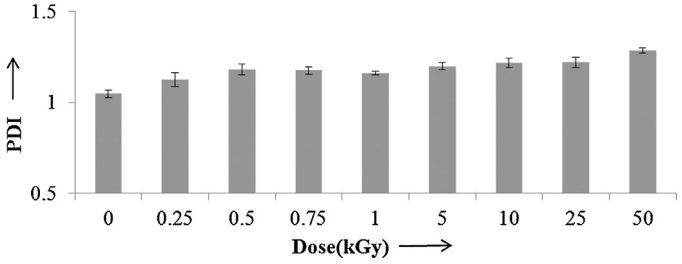

Fig. 4. Effect of gamma irradiation on polydispersity index (PDI) of GG.

Table 1
Effect of gamma irradiation on mechanical and barrier properties and color co-ordinates of guar gum films. Films prepared from irradiated guar gum.

Dose (kGy)	Tensile strength (MPa)	Young's Modulus (MPa)	Puncture strength (N)	% Elongation	Water vapor transmission rate ($gm/m^2/day$)	L^* (Black to white)	a^* (Green to magenta)	b^*(Blue to yellow)	Opacity (%)
0	60.5 ± 8.7^{bc}	162 ± 23^{a}	2.3 ± 0.2^{a}	13.9 ± 4.5^{b}	190 ± 10^{ab}	97.7 ± 0.8^{a}	0.8 ± 0.2^{c}	1 ± 0.1^{d}	12.9 ± 0.2^{d}
0.25	71.4 ± 10.6^{ab}	151 ± 39^{a}	1.93 ± 0.2^{b}	22.8 ± 3.8^{a}	186.9 ± 8.3^{abc}	94.4 ± 0.8^{d}	2.3 ± 0.3^{a}	1.9 ± 0.2^{f}	15.2 ± 0.5^{a}
0.5	80.2 ± 13.9^{a}	158 ± 16^{a}	1.8 ± 0.2^{b}	18.6 ± 1.9^{ab}	192.5 ± 12^{ab}	94.4 ± 0.9^{d}	1.6 ± 0.3^{b}	1.7 ± 0.2^{f}	13.4 ± 0.5^{cd}
0.75	58.6 ± 7.8^{bc}	149 ± 11^{a}	1.69 ± 0.1^{b}	19.4 ± 2.5^{ab}	195.7 ± 12^{ab}	96.1 ± 0.7^{bc}	0.1 ± 0.01^{ef}	$0.2 \pm .04^{b}$	13.3 ± 0.5^{cd}
1	55 ± 6.2^{c}	154 ± 19^{a}	1.6 ± 0.3^{b}	14.7 ± 1.2^{b}	184 ± 7.5^{abc}	97.2 ± 0.6^{ab}	$.03 \pm .02^{ef}$	$0.3 \pm .04^{b}$	12.9 ± 0.3^{d}
5	26.7 ± 5.3^{d}	65 ± 19^{b}	1.7 ± 0.3^{b}	18.4 ± 2.4^{ab}	170 ± 4.4^{cd}	98.3 ± 0.8^{a}	0.2 ± 0.1^{de}	0.7 ± 0.1^{c}	13.2 ± 0.7^{cd}
10	22.4 ± 3.8^{de}	63 ± 11^{b}	1.2 ± 0.1^{c}	19.1 ± 3.3^{ab}	175.6 ± 8^{bcd}	94.8 ± 0.7^{cd}	0.1 ± 0.04^{f}	0.9 ± 0.04^{a}	14.3 ± 0.3^{b}
25	19.32 ± 4.5^{de}	49 ± 12^{b}	1.0 ± 0.2^{c}	16.1 ± 1.6^{b}	177.5 ± 9^{bcd}	96 ± 0.7^{bc}	0.42 ± 0.04^{d}	0.8 ± 0.1^{c}	13.9 ± 0.3^{bc}
50	7.8 ± 2.5^{e}	35 ± 11^{b}	0.8 ± 0.2^{c}	7.8 ± 2.5^{c}	160.6 ± 5.2^{d}	96.1 ± 0.6^{bc}	0.7 ± 0.2^{c}	1.4 ± 0.1^{e}	13.8 ± 0.4^{bc}

Any two means in the same column followed by the same letter are not significantly ($p > 0.05$) different.

tomannans significantly affects the mechanical properties of the films. For example, films prepared from the locust bean gum (M/G ratio of approximately 3.33) were stronger and more flexible than films prepared from control GG (M/G ratio of approximately 1.67) (Mikkonen et al., 2007).

3.2. Effect of radiation on mechanical properties of GG based films

GG films were prepared from control and irradiated samples in powder form. Films prepared from unirradiated unpurified GG demonstrated thickness of 13.66 ± 3.3 μm, tensile strength of 6 ± 1.1 MPa and Young's modulus of 63 ± 12 MPa. While that from purified GG demonstrated an improved tensile strength of 60.5 ± 8.7 MPa and Young's modulus of 162 ± 23 MPa with thickness of 14.33 ± 2.3 μm. In a previous study on GG based films the tensile strength of control GG plasticized with 40% glycerol (w/w of GG) was reported to be 12 MPa (Mikkonen et al., 2007). Films prepared from other galactomannans such as locust bean gum were reported to have a tensile strength of 35 MPa (Aydinli et al., 2004). A substantial improvement in tensile strength and Young's modulus of films observed here might be due to the additional purification step followed in this study, which leads to removal of insoluble impurities from GG. Impurities mainly consisted of high molecular weight macromolecules, proteins and arabinose and glucose residues (Cunha, Paula, & Feitosa, 2007). This could lead to a uniform and compact packing of GG polymer chains in the films prepared, resulting in increased tensile strength. Thus, all further work was performed on purified GG. However, no statistically significant effect of purification was observed on film thickness.

Radiation processing had a significant ($p < 0.05$) effect on the tensile strength of GG films. Interestingly, an increase in tensile strength to 80.2 ± 13.9 MPa up to a dose of 500 Gy with dose dependent decrease, thereafter, was observed (Table 1). The tensile strength of GG films reduced to 7.8 ± 2.5 MPa at a dose of 50 kGy. Kim et al. (2008) reported an increase in tensile strength by 27.5% of starch and locust bean gum combination films at irradiation dose of 3 kGy. An increased tensile strength for starch based plastics sheets at irradiation dose of 30–70 kGy with a dose dependent decrease at higher doses (>70 kGy) was also reported by Zhai, Yoshii, and Kume (2003). For pectin-based films, an increase in tensile strength by 31.2% at a dose of 10 kGy with a decrease at higher doses was reported earlier (Jo, Kang, Lee, Kwon, & Byun, 2005). Improved tensile strength due to irradiation in previous studies was attributed to radiation induced cross-linking of polymers, while reduction in tensile strength at higher doses was reported to have occurred due to radiation induced degradation of polymers (Byun et al., 2008). An increase in tensile strength of GG based films due to enzymatic depolymerization because of increased solubility and better orientation of short chain polymer was previously reported (Mikkonen et al., 2007). Surprisingly, no increase in tensile strength was observed due to radiation induced depolymerization in the present study. This might be due to the fact that radiation depolymerization resulted in different molecular weight distributions as compared to enzymatic depolymerization. In the present study, a dose dependent increase in PDI was observed thus suggesting a wide molecular weight distribution of irradiated GG samples. Further, even at a high radiation dose of 50 kGy presence of higher Mw fractions was demonstrated by GPC studies (Fig. 2c). Due to the presence of higher Mw fractions and wide molecular weight distribution, a restriction in the ordering of polymer chains is expected that could possibly decrease tensile strength. Interestingly, at a lower irradiation dose of 500 Gy 32.6 percent increase in tensile strength was observed (Table 1). These changes could possibly be due to conformational change in GG particle structure, which was further confirmed by SAXS.

Young's modulus is a measure of stiffness of any sample. Films prepared with irradiated GG demonstrated no statistically significant ($p < 0.05$) difference in Young's modulus up to a dose of 1 kGy. However, a dose dependent decrease was noted thereafter (Table 1). A decrease in Young's modulus signifies a reduction in stiffness of films i.e. films prepared become more amenable to deformation.

GG films prepared from control samples were also directly subjected to irradiation processing and its impact on their tensile strength is shown in Table 2. No significant ($p < 0.05$) impact on tensile strength and Young's modulus was observed due to radiation processing up to a dose of 25 kGy and 50 kGy, respectively. Beyond these doses the tensile strength and Young's modulus showed a dose dependent decrease (Table 2). This decrease was however lesser when films were directly irradiated compared to films prepared from irradiated GG.

Effect of radiation on puncture strength of films was also evaluated. Puncture strength of control GG films was 2.3 ± 0.2 N. A radiation dose dependent decrease in puncture strength of GG films was observed. The puncture strength reduced to 1.2 ± 0.1 N at 10 kGy, and thereafter to 0.8 ± 0.2 N at 50 kGy (Table 1). Films prepared from control GG and subjected to irradiation processing demonstrated no significant change in puncture strength up to a dose of 10 kGy; however it decreased to 1.6 ± 0.3 N and 0.9 ± 0.1 N at 25 kGy and 100 kGy, respectively (Table 2).

Percent elongation indicates the flexibility of films. The films prepared from non-irradiated GG demonstrated 13.9 ± 4.5 percent elongation. In a previous study on GG films (Mikkonen et al., 2007), percent elongation was observed to be 40 percent. In the present study, GG was purified to remove all insoluble impurities before film preparation. This might have resulted in decreased percent elongation. No trend was observed on the percent elongation of films prepared from irradiated GG and for GG films subjected directly to irradiation (Tables 1 and 2). Similar results were also found for percent elongation by Zhai et al. (2003), for irradiation of

Table 2
Effect of irradiation on mechanical and barrier properties and color co-ordinates of guar gum films. Films prepared from control guar gum and irradiated thereafter.

Dose (kGy)	Tensile strength (MPa)	Young's modulus (MPa)	Puncture strength (N)	% Elongation	Water vapor transmission rate (gm/m^2/day)	L^* (Black to white)	a^* (Green to magenta)	b^*(Blue to yellow)	Opacity (%)
0	60.5 ± 8.7^{a}	162 ± 23^{a}	2.3 ± 0.2^{a}	13.9 ± 4.5^{ab}	190 ± 10^{a}	97.2 ± 0.6^{a}	0.6 ± 0.2^{a}	1.1 ± 0.2^{f}	12.9 ± 0.2^{d}
1	51.9 ± 1.1^{a}	158 ± 33^{a}	2.1 ± 0.1^{a}	12 ± 3.9^{ab}	190.8 ± 11.1^{a}	95 ± 0.6^{b}	$.02 \pm .01^{e}$	0.3 ± 0.1^{c}	13.8 ± 0.4^{ab}
5	55.9 ± 4.5^{a}	177 ± 36^{a}	2.3 ± 0.2^{a}	12.3 ± 5.5^{ab}	188.3 ± 8^{a}	94.7 ± 0.4^{b}	0.4 ± 0.1^{bc}	0.7 ± 0.1^{e}	13.3 ± 0.3^{cd}
10	51.8 ± 5.2^{a}	148 ± 25^{ab}	2 ± 0.3^{ab}	15 ± 0.9^{ab}	185.6 ± 6.2^{ab}	94.8 ± 0.8^{b}	0.2 ± 0.1^{de}	$.04 \pm .02^{d}$	13.5 ± 0.2^{bc}
25	58.5 ± 3.8^{a}	166 ± 29^{a}	1.6 ± 0.3^{bc}	18.5 ± 5.1^{a}	192.9 ± 3.8^{a}	93.7 ± 0.4^{bc}	0.3 ± 0.1^{cd}	$0.3 \pm .01^{c}$	14.2 ± 0.3^{a}
50	43.1 ± 1.2^{b}	151 ± 29^{ab}	1.4 ± 0.3^{c}	9.3 ± 1.7^{b}	183.9 ± 4.7^{ab}	93 ± 0.4^{c}	0.5 ± 0.1^{ab}	$.01 \pm .01^{d}$	13.2 ± 0.1^{cd}
100	40.9 ± 5.3^{b}	101 ± 20^{b}	0.9 ± 0.1^{d}	17.5 ± 3.6^{a}	181 ± 6.5^{ab}	93.3 ± 1^{c}	0.7 ± 0.1^{g}	3.1 ± 0.2^{a}	14.1 ± 0.2^{a}

Any two means in the same column followed by the same letter are not significantly ($p > 0.05$) different.

starch based plastic film. Thus, our results are in concurrence with earlier studies.

3.3. Characterization of guar gum by small angle X-ray scattering (SAXS)

Conformation of unirradiated and irradiated (500 Gy and 50 kGy) GG was analyzed by small angle X-ray scattering. The SAXS profiles for the control and different dose treated polymer are shown in Fig. 5. In the present case, the interpretation the SAXS scattering data is based on the analysis of the scattering curve, which showed the dependence of the scattering intensity, I, on the scattering wave vector q. The scattered intensity as a function of q for the three solutions (Fig. 5), shows a power law behavior [$I(q) \sim q^{-d}$]. The slope of the linear region in $\log I(q)$ vs. $\log q$ plot gives the value of the exponent d, the dimensionality of the scattering object. Typically, the exponent $d = 2$ is exhibited by Gaussian chains in case of polymer. The scattering curve for the control polymer and 50 kGy treated polymer show a q^{-2} dependence in the experimental q range. However, for the 500 Gy dose treated polymer, in addition to the q^{-2} dependence a prominent peak at high q is also observed (Fig. 5). This prominent peak probably arises due to correlations of short length scales, with the inter-chain correlation length, $\xi = 2\pi/q^*$(where q^* is the peak position). The peak position was found to be 1.74 nm^{-1}.The correlation length ξ was calculated as 3.6 nm. The scattering profile for control and 50 kGy treated polymer is modeled by assuming Gaussian coiled chain, the formula used for (Eq. (9)):

$$Igc(q) = \frac{2\left[\exp(-q^2R_g^2) - 1 + q^2R_g^2\right]}{q^4R_g^4} \quad (9)$$

where R_g is the typical chain length of the polymer.

To account the ordering of the polymer treated up to 500 Gy, a hard sphere structure factor $S(\varphi, r_{hs})$ (Pedersen, 1994) was taken into account where φ is the local packing fraction of the polymer and $2r_{hs}$ is the typical correlation length. The scattering intensity for the 500 Gy treated polymer can be written as:

$$I(q) = Igc(q) \times S(\varphi, r_{hs}) \quad (10)$$

It is evident from Fig. 5 that above discussed model fit the data quite satisfactorily. The typical chain length R_g for all the specimens was found to be ~ 20 nm. The correlation length $2r_{hs}$ was found to be 3.2 nm which is approximately same as that estimated from the peak position (ξ). The local packing fraction of the chain is found to be 0.22. Thus, it is clear from the SAXS analysis the conformation of the GG polymer chain do not undergo modification under different radiation doses under present probed length scale. However, for lower dose of 500 Gy, the ordering of the chains occurs with typical correlation length of 3.6 nm and local packing fraction of 0.22. Thus, the possibility of ordering of chains resulting in better orientation of GG polymers during film formation and increased tensile strength at lower dose up to 500 Gy is suggested.

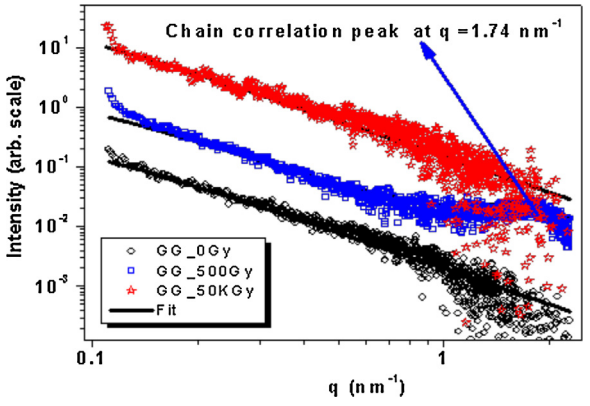

Fig. 5. The small angle X-ray scattering (SAXS) profiles of the control and irradiated (500 Gy, 50 kGy) GG.

3.4. Effect of radiation on water vapor transmission rate of guar gum based films

WVTR of control GG films was 190 ± 10 gm/m^2/day. Aydinli et al. (2004) found water vapor transmittance rate for locust bean gum plasticized with PEG 200 and PEG 1000 to be 251 gm/m^2/day and 136 gm/m^2/day, respectively. Radiation significantly ($p < 0.05$) affected WVTR of films. Films made from irradiated GG powder had WVTR of 160.6 ± 5.2 gm/m^2/day at 50 kGy (Table 1). Thus, an enhanced barrier to water vapor was noted in GG films prepared from GG powder irradiated at higher doses with no significant effect at doses less than 1 kGy. No significant effect of radiation was observed on the WVTR of films prepared from non-irradiated GG and subjected to irradiation processing thereafter (Table 2). These results are in good agreement with Kim et al. (2008) who concluded that radiation treatment of biomaterials may result in more compact structure (because of lower molecular weight fragments) and could help natural polymers to overcome their hydrophilic character.

3.5. Color and opacity of guar gum films

Values for color coordinates i.e. L^*, a^* and b^* are shown in Tables 1 and 2. No significant ($p < 0.05$) differences were obtained in L^* values for films prepared with irradiated guar gum. Films prepared with GG irradiated at lower doses up to 500 Gy demonstrated slightly higher a^* values as compared to control films indicating increased redness of films. However at higher doses beyond 500 Gy a^* values were comparable to that of control. No statistical significant ($p < 0.05$) difference was obtained in b^* values for films prepared with irradiated GG. For films prepared with control GG and subjected to radiation processing thereafter a significant dose dependent reduction in L^* values were observed indicating

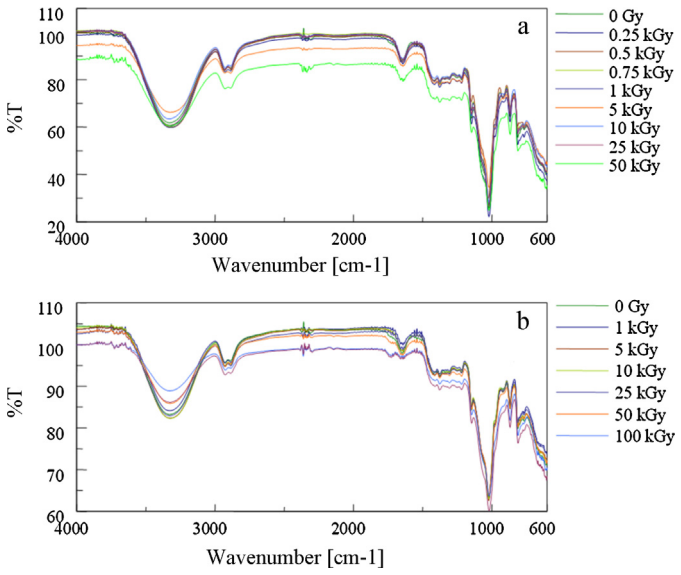

Fig. 6. FTIR profiles of GG films: (a) films prepared from irradiated GG; (b) control GG films then subjected to irradiation.

increased darkness of films. At very high doses of 100 kGy increased b^* values were observed. Increase in b^* values indicate increase yellowness of films. Jo et al. (2005) also reported similar results for irradiated pectin and gelatin based films i.e. with dose decrease in L^* and a^* values and increase in b^* values.

Opacity indicates degree to which light is not allowed to pass through. Opacity of packaging films is important as it affect the packaged products visibility to consumers. A significantly higher opacity was observed in films prepared with irradiated GG as well as films subjected to radiation processing after preparation, as compared to control samples. Observed increase in opacity might be due to increased darkness or redness in irradiated samples. Although, significant variance was observed instrumentally in color and opacity of samples after irradiation visual differences were negligible to be discerned by naked eye.

3.6. FTIR analysis of films

To compare the changes in chemical structure of control and gamma irradiated guar gum films, FTIR spectra was recorded. Fig. 6 shows FTIR spectra of control as well as irradiated gaur gum films. IR spectra of films prepared with irradiated GG and films subjected to radiation processing after preparation were superimposable with control films. Gupta et al. (2009) reported no change in FTIR spectrum of control and irradiated guar gum. Above results suggests that during radiation processing there are no major functional group transformations but only random free radical chain scission in GG due to irradiation.

4. Conclusion

Radiation processing of GG resulted in decrease in molecular weight of GG as analyzed by Ostwald viscometer and gel permeation chromatography. No significant change was observed in mannose:galactose ratio of GG due to radiation processing. Enhanced tensile strength of GG films was observed in the present study as compared to reported values in literature due to the purification procedure followed. Irradiation of GG in powder form up to 500 Gy resulted in 32.6% increase in tensile strength of its films. SAXS studies demonstrated that partial ordering of the polymer chains at a low dose of 500 Gy resulted in an increase in tensile strength. A dose dependent decrease in tensile and puncture strength of films was observed. Films prepared from unirradiated GG and subjected to irradiation processing thereafter exhibited stability up to 25 kGy without significant loss in its mechanical and barrier properties. Thus, these films can be suitably employed for food irradiation applications without loss of functionality. In conclusion, purification of GG combined with low dose irradiation can improve the mechanical properties of the films produced by it.

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